Supporting Information

General

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. (S)-1-octyn-3-ol and 1-propyn-3-ol were purchased from Aldrich and protected with t-butyldimethylsilyl chloride under standard conditions. 7-hydroxyhept-5-ynoate [G. Casy, J. W. Patterson, R. J. K. Taylor, *Org. Synth. Collect. Vol. VIII*, **1993**, 415-420], 1-hydroxy-4-phenyl-2-butyne [a) G. G. Pegg, G. G., G. V. Meehan, *Aust. J. Chem.* **1990**, *43*, 1789-1790; b) A. Claeson, C. Sahlberg, *Tetrahedron* **1982**, *38*, 363-368], and (*R*)-(+)-4-(t-butyldimethysilyloxy)-2-cyclopenten-1-one [a) T. T. Curran, D. A. Hay, C. P. Koegel, *Tetrahedron* **1997**, *53*, 1983-2004; b) L. A. Paquette, M. J. Earle, G. F. Smith, *Org. Synth*. **1995**, *73*, 36-43; c) L. A. Paquette, T. M. Heidelbaugh, *Org. Synth*. **1995**, *73*, 44-49] were prepared according to literature procedures. Tetrahydrofuran (THF) was distilled under N_2 from sodium/benzophenone immediately before use. All reactions were run under an inert atmosphere with dry reagents and solvents and flame-dried glassware. Flash column chromatography was carried out using Merck 60 230-400 mesh silica gel. Thin layer chromatography was performed using 0.25 mm silica gel coated Kieselgel 60 F_{254} plates and visualized using aqueous cerium molybdate with heating. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at 400 MHz and 100 MHz respectively, in [D]$CHCl_3$ at 25 °C. Chemical shifts are reported in ppm on the δ scale from an internal TMS standard. High-performance liquid chromatography (HPLC) was conducted using a C-18 column (VYDAC TP54, 5 μm, 25 cm) at room temperature and the following: gradient mobile phase, 20% acetonitrile/water (maintained 5 min) to 80% acetonitrile/water (during 35 min, and maintained 20 min); flow rate, 1.0 mL/min; detection, ELSD (Evaporative Light Scattering Detector, Alltech 500).

Polymer-Supported and Library Synthesis

Polymer 3a (typical procedure). A dry 10 mL round bottom flask (rbf) was charged with zirconocene hydride chloride (0.39 g, 1.5 mmol) followed by anhydrous THF (6 mL) and 1-octyne (0.222 mL, 1.5 mmol). The suspension was shielded from light by wrapping in aluminum foil and allowed to stir for 30 min at room temperature. The homogeneous solution was cooled to -50 °C, treated with MeLi (1.4 M in hexane, 2.14 mL, 3.0 mmol) and stirred at -50 °C for 10 min. The mixture was transferred to a pre-cooled (-50 °C) 25 mL rbf containing CuCN (0.134 g, 1.5 mmol) and stirred for 15 min at -50 °C followed by the addition of MeLi (1.4 M in hexane, 1.07 mL, 1.5 mmol). The mixture was stirred for 15 min at -50 °C to generate a brown cuprate solution. To the cuprate was added a solution of polymer **1** (1.0 g, 0.3 mmol) in dry THF (12 mL) at -50 °C. It should be noted that the mixture became rather thick. After 40 min at -50 °C, chlorotrimethylsilane (0.94 mL, 7.5 mmol) was added dropwise to afford a clear solution and stirring was continued for 30 min before triethlyamine (2.1 mL, 15 mmol) was added. The mixture was allowed to warm to 0 °C and stirring was continued for 15 min and then poured into a mixture of saturated aqueous ammonium chloride/ammonium hydroxide (9/1, 50 mL) and 50 mL of ethyl acetate. The quenched mixture was stirred for 2 h at room temperature and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and filtered. After removal of solvent, the residue was dissolved in ethyl acetate and filtered through a pad of Celite to give a thick oil. The product bound polymer was obtained utilizing the following standard procedure: The oil was dissolved in a small amount of THF (6 mL) and the polymer-supported product was precipitated by adding the THF solution to a cooled solution of methanol (-30 °C). The polymer was filtered, washed thoroughly with methanol, dried under vacuum and obtained as a white solid (0.82 g, 80% polymer recovered).

^{1}H NMR: δ = 0.21 (s, 9H; $SiCH_3$), 0.87 (m, 3H; CH_3), 4.47 (m, 2H; $ArCH_2O$), 4.52 (s, 1H; CH=COTMS), 4.98 (m, 1H; OCHO), 5.4-5.5 (m, 2H; vinyl). Signals in the range δ = 1.2-

2.3 and 6.2-7.3 ppm overlapped with that of the polymer that precluded definitive ^{1}H NMR assignments.

Polymers **3b**, **3c** and **3d** were prepared from **2b**, **2c**, and **2d** respectively following the same procedure.

3b: ^{1}H NMR: δ = 0.05-0.3 (m, 15H; $SiCH_3$), 0.86 (m, 12H; CH_3), 4.05, (m, 1H; CHOTBS), 4.47 (m, 2H; $ArCH_2O$), 4.52 (s, 1H; CH=COTMS), 4.95 (m, 1H; OCHO), 5.4-5.65 (m, 2H; vinyl).

3c: ^{1}H NMR: δ = 0.05-0.3 (m, 15H; $SiCH_3$), 0.90 (m, 9H; CH_3), 4.15 (m, 2H; CH_2OTBS), 4.48 (m, 2H; $ArCH_2O$), 4.55 (s, 1H; CH=COTMS), 4.98 (m, 1H; OCHO), 5.5-5.8 (m, 2H; vinyl).

3d: ^{1}H NMR: δ = 0.3 (s, 9H; $SiCH_3$), 3.33 (m, 2H; CH_2Ph), 4.48 (m, 2H; $ArCH_2O$), 4.52 (s, 1H; CH=COTMS), 4.98 (m, 1H; OCHO), 5.5-5.85 (m, 2H; vinyl).

Triflate 4a (typical procedure). The triflate was prepared just before use. A dry 25 mL rbf was charged with trifluoromethanesulfonic anhydride (0.55 mL, 3.3 mmol) and cooled to -23 °C. A mixture of 2-butyn-1-ol (0.224 mL, 3.0 mmol) and 2,6-di-t-butylpyridine (0.8 mL, 3.6 mmol) in 3 mL of dichloromethane was added dropwise over 3 min and stirring was continued for 10 min at -23 °C. The mixture was treated dropwise with hexane (10 mL) and then cooled to -78 °C with vigorous stirring for 10 min. The thick suspension was filtered through a pad of anhydrous sodium sulfate into a precooled (-78 °C) 25 mL flask and the pad rinsed with 3 mL of hexane. The filtrate was quickly concentrated to 2-3 mL at < 0 °C, cooled to -78 °C and 3 mL of dry THF were run down the side of the flask. The solution was purged with argon and kept at -78 °C until used.

Pool 5A (typical procedure for α-alkylation). A mixture of polymers **3a**, **3b**, **3c**, and **3d** (50 mg each, 0.06 mmol) was dissolved in dry THF (8 mL), purged with argon and placed in a cooling bath at -23 °C. The solution was treated with MeLi (1.4 M in hexane, 0.17 mL, 0.24

mmol) added in one portion. Stirring was continued for 40 min at -23 °C and then the yellow solution was rapidly cooled to -78 °C and treated with the freshly prepared triflate **4a** solution (1.08 mmol) *via* cannula. The resulting solution was stirred for 10 min at -78 °C and for 40 min at -23 °C, quenched by the addition of saturated aqueous ammonium chloride (5 mL) and allowed to warm to room temperature. The mixture was poured into 30 mL of saturated aqueous ammonium chloride and extracted with 50 mL of ethyl acetate. The organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated. The polymer-supported product was obtained as a solid using the standard procedure (*vide supra*).

^{1}H NMR: δ = 4.95 (m, 1H; OCHO), 5.3-5.9 (m, 2H; vinyl).

Pools **5B**, **5C**, and **5D** were prepared from triflates **4b**, **4c**, and **4d** respectively following the same procedure.

5B: ^{1}H NMR: δ = 2.19 (m, 2H; $CH_2C{\equiv}C$), 2.41 (m, 2H; $CH_2C{\equiv}C$), 3.65 (s, 3H; CO_2CH_3), 4.98 (m, 1H; OCHO), 5.3-5.8 (m, 2H; vinyl).

5C: ^{1}H NMR: δ = 1.1 (t, 3H; CH_3), 4.96 (m, 1H; OCHO), 5.4-5.9 (m, 2H; vinyl).

5D: ^{1}H NMR: δ = 3.6 (s, 2H; $C{\equiv}CCH_2Ph$), 5.0 (m, 1H; OCHO), 5.3-5.7 (m, 2H; vinyl).

Pool 6A (typical procedure for reduction). **Pool 5A** (0.15 g, 0.045 mmol) was dissolved in benzene (2 mL) and cyclohexane (2 mL). To the solution was added quinoline (0.3 g) and 5% palladium on barium sulfate (0.3 g) and the mixture stirred under hydrogen (1 atm) at 45 °C for 48 h. The mixture was filtered through a pad of Celite and the filtrate evaporated. The polymer-supported product (0.135 g, 90% polymer recovered) was obtained as a solid using the standard procedure (*vide supra*).

^{1}H NMR: δ = 4.94 (m, 1H; OCHO), 5.3-5.8 (m, 4H; vinyl).

Pools **6B**, **6C**, and **6D** were prepared from **5B**, **5C**, and **5D** respectively, following the same procedure.

6B: ^{1}H NMR: δ = 2.24 (m, 2H; $CH_2C{=}C$), 3.67 (s, 3H; CO_2CH_3), 4.85 (m, 1H; OCHO), 5.3-5.7 (m, 4H; vinyl).

6C: ^{1}H NMR: δ = 4.95 (m, 1H; OCHO), 5.2-5.8 (m, 4H; vinyl).

6D: ^{1}H NMR: δ = 3.34 (m, 2H; C=CCH_2Ph), 4.9 (m, 1H; OCHO), 5.3-5.8 (m, 4H; vinyl).

Pool 1 (typical procedure for cleavage from polymer). A solution of **pool 6A** (0.11 g, 0.03 mmol) in THF (2 mL) was treated with 48% aqueous hydrofluoric acid (0.2 mL). The mixture was stirred at 45 °C for 6 h and neutralized with saturated sodium bicarbonate solution. The aqueous layer was extracted with ethyl acetate and the organic solution was washed with saturated sodium bicarbonate, brine and dried over anhydrous sodium sulfate and then concentrated. To the residue was added a small amount of THF (0.1 mL) and MeOH (10 mL) and the mixture cooled to -30 °C with vigorous stirring to precipitate the polymer. After removal of the polymer, the filtrate was concentrated to give the prostaglandin library (**pool 1**) (3.2 mg, 38% based on an average of molecular weights).

^{1}H NMR: δ = 2.79 (m, 1H; CH_2C=O), 3.38 (m, 1H; CH_2O and CH_2Ph), 4.10 (m, 1.25H; CHO in ring and ω chain), 5.28-5.84 (m, 4H; vinyl), 7.1-7.4 (m; phenyl).

HPLC (retention time, min): 6.98 (**7ac**), 26.47 (**7ab**), 31.28 (**7ad**), 36.70 (**7aa**).

Pool 2 (3.3 mg, 37%), **pool 3** (2.8 mg, 33%), and **pool 4** (2.4 mg, 26%) were prepared from **6B**, **6C**, and **6D** respectively, following the same procedure.

Pool 2: ^{1}H NMR: δ = 2.71 (m, 1H; CH_2C=O), 3.41 (m, 1H), 3.65 (s, 3H; CO_2CH_3), 4.1 (m, 1.25H), 5.31-5.76 (m, 4H), 7.12-7.26 (m; phenyl).

HPLC (retention time, min): 17.57, 26.07 (PGE_2 methyl ester), 35.36, 35.88.

Pool 3: ^{1}H NMR: δ = 2.77 (m, 1H; CH_2OC=O), 3.35 (m, 1H), 3.7 (m, 0.7H), 4.1 (m, 0.5H), 5.20-5.90 (m, 4H; vinyl), 7.15-7.31 (m; phenyl).

HPLC (retention time, min): 12.56, 28.58, 31.30, 38.90.

Pool 4: ^{1}H NMR: δ = 2.82 (m, 1H; CH_2C=O), 3.5 (m, 3H; CH_2O and CH_2Ph in ω chain and C=CCH_2Ph in α chain), 4.20 (m, 1.25H), 5.38-5.85 (m, 4H; vinyl), 7.1-7.4 (m; phenyl)

HPLC (retention time, min): 19.00, 25.70, 34.82, 41.44.

Notes for ^{1}H NMR analysis. At each stage, not all prostanoid signals were identifiable because of interferences from polymer resonances or because of complexity of the mixture. However, there were significant marker resonances that allowed assignments and confirmation of reactions and pool chemical composition. The vinyl group relative integrations of polymer-supported compounds in **pools 6A-D** were doubled compared with those in **pools 5A-D** that indicated success of the reduction step. The methyl ester signal in **pool 2**, the terminal methyl signal in **pool 3**, and the distal methylene signal in **pool 4** were observed that confirmed the incorporation of the α chain. In **pools 1-4**, the ring α hydrogens, hydrogens on hydroxyl functionalized carbons, and the vinylic hydrogens were clearly observed.

Notes for HPLC analysis. Polymer-supported compounds that had no α chains (**3a**, **3b**, **3d**) were cleaved from the polymer and analyzed by HPLC (retention time, min: 29.7, 18.1, 21.2). The compound derived from **3c** was very water soluble and could be eliminated during workup. These compounds served to verify the conversion of pool ω into fully functionalized prostanoids. At the final stage, the composition of **pool 1** was confirmed by comparison to the retention times of authentic compounds **7aa**, **7ab**, **7ac**, and **7ad** prepared individually in solution (**7ad** could only be prepared by polymer-supported synthesis) as well as by coinjection of **pool 1** and the mixture of the individual compounds. Peaks corresponding to the monosubstituted compounds (ω chain) were not evident in **pool 1** but were observed in minor amounts in other pools. Compound **7ac** showed a smaller response factor (~25%) than **7aa**, **7ab**, and **7ad**. Based on the reduced peak height and the similarity in retention times, all compounds in other pools containing the ω chain derived from **2c** were assigned. Similarly, HPLC peaks of other compounds from **pools 2-4** were assigned by comparison to the HPLC traces of **pool 1** and the monosubstituted compounds. A polymer by-product was observed upon HPLC that varied in concentration between polymer lots of **1**.

Solution-Phase Synthesis

(refer to scheme 1)

Compound 11a (typical procedure). A dry 10 mL rbf was charged with zirconocene hydride chloride (0.27 g, 1.0 mmol), anhydrous THF (4 mL) and 1-octyne (0.15 mL, 1.0 mmol). The suspension was shielded from light with aluminium foil and allowed to stir for 30 min at room temperature. The homogeneous solution was cooled to -50 °C, treated with MeLi (1.4 M in hexane, 1.43 mL, 2.0 mmol) and stirred at -50 °C for 10 min. The mixture was transferred to a precooled (-50 °C) 25 mL flask containing CuCN (0.09 g, 1.0 mmol), and stirred for 15 min at -50 °C, followed by the addition of MeLi (1.4 M in hexane, 0.71 mL, 1.0 mmol). The mixture was stirred for 15 min at -50 °C to generate a brown cuprate solution. To the cuprate was added a solution of (*R*)-(+)-4-(t-butyldimethysilyloxy)-2-cyclopenten-1-one (0.106 g, 0.5 mmol) in dry THF (2 mL) and stirred for 15 min at -50 °C. Chlorotrimethylsilane (0.32 mL, 2.5 mmol) was added dropwise, stirring was continued for 15 min at -50 °C, and triethylamine (0.7 mL, 5.0 mmol) was added. The cooling bath was removed, and the mixture was allowed to warm to 0 °C and then poured into a mixture of 25 mL of distilled water and 50 mL of diethyl ether. The aqueous layer was extracted with 50 mL of ether and the combined organic solutions were washed with brine, dried over anhydrous sodium sulfate and filtered through a pad of Celite. The solvent was removed to give the silylenol ether **10a** as a pale yellow oil. In the ^{1}H NMR, the enolic proton was observed near 4.4 ppm.

The above crude silylenol ether (0.5 mmol) in a 25 mL flask was dissolved in dry THF (4 mL), purged with argon and placed in a cooling bath at -23 °C. The solution was treated with MeLi (1.4 M in hexane, 0.54 mL, 0.75 mmol) added in one portion. Stirring was continued for 15 min at -23 °C and then the yellow solution was immediately cooled to -78 °C and treated with the freshly prepared triflate **4a** solution (3.0 mmol) *via* cannula. The resulting solution was

stirred for 10 min at -78 °C and for 20 min at -23 °C and then quenched by the addition of saturated aqueous ammonium chloride (5 mL) and allowed to warm to room temperature. The mixture was poured into 30 mL of saturated aqueous ammonium chloride and extracted with 100 mL of ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate and then concentrated. The residue was chromatographed eluting with ethyl acetate/hexane (1/15) to give the product as a colorless oil (44 mg, 24%).

^{1}H NMR: δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.85 (m, 12H), 1.2-1.4 (m, 8H), 1.74 (t, ^3J (H,H) = 2.5 Hz, 3H; C≡CCH_3), 1.96-2.06 (m, 3H), 2.15-2.28 (m, 2H), 2.55-2.71 (m, 3H), 4.03 (q, ^3J (H,H) = 8.7 Hz, 1H; CHO), 5.27 (m, 1H), 5,64 (m, 1H).

^{13}C NMR: δ = -4.7, 3.6, 14.1, 16.6, 18.1, 22.6, 25.6, 28.9, 29.3, 31.7, 32.7, 47.6, 52.7, 53.1, 73.1, 75.4, 128.9, 134.5, 214.2.

ESMS: *m*/*z* (%): 399 (100) [M+Na^+], 415 (68) [M+K^+].

11b: ^{1}H NMR: δ = 0.04, 0.05, 0.06 (each s, 12H), 0.88 (m, 21H), 1.24-1.34 (m, 6H), 1.39-1.46 (m, 2H), 1.75 (t, ^3J (H,H) = 2.4 Hz, 3H; C≡CCH_3), 1.98 (q, ^3J (H,H) = 4.8 Hz, 1H), 2.16-2.25 (m, 2H), 2.59-2.67 (m, 2H), 2.74-2.81 (m, 1H), 4.08 (m, 2H; CHO), 5.48-5.54 (m, 1H), 5.65 (dd, ^3J (H,H) = 15.4, 5.2 Hz, 1H).

FABMS: *m*/*z* (%): 507 (7) [M+H^+], 529 (45) [M+Na^+]; HRMS calcd for $C_{29}H_{54}O_3Si_2Na$ 529.3509, found 529.3503.

11c: ^{1}H NMR: δ = 0.03, 0.04, 0.06 (each s, 12H), 0.87, 0.89 (each s, 18H), 1.74 (m, 3H; C≡CCH_3), 2.05-2.28 (m, 3H), 2.49-2.62 (m, 2H), 2.74-2.81 (m, 1H), 4.05-4.17 (m, 3H; CHO, CH_2O), 5.53-5.77 (m, 2H).

ESMS: *m*/*z* (%): 459 (85) [M+Na^+], 475 (12) [M+K^+].

Compound 12a (typical procedure for reduction). A mixture of **11a** (27 mg, 0.072 mmol), 5% palladium on barium sulfate (40 mg), quinoline (40 mg), benzene (2 mL) and cyclohexane (2 mL) was stirred under hydrogen (1 atm) at room temperature for 2.5 h and at 40 °C for 4 h. The catalyst was filtered through a pad of Celite and the filtrate evaporated. The

residue was chromatographed eluting with ethyl acetate/hexane (1/15) to give the product as a colorless oil (21 mg, 62%).

^{1}H NMR: δ = 0.02, 0.03 (each s, 6H), 0.86 (m, 12H), 1.27-1.42 (m, 8H), 1.58 (dd, ^3J (H,H) = 18.2, 6.2 Hz, 3H; C=CCH_3), 2.02-2.19 (m, 5H), 2.31-2.42 (m, 2H), 2.60 (m, 1H), 3.98 (q, ^3J (H,H) = 8.7 Hz, 1H; CHO), 5.23-5.57 (m, 4H; vinyl).

^{13}C NMR: δ = -4.7, 12.9, 14.1, 22.6, 24.4, 25.7, 28.9, 29.3, 31.7, 32.7, 47.7, 53.4, 54.2, 73.1, 125.9, 126.5, 129.7, 134.1, 215.7.

ESMS: *m*/*z* (%): 401 (100) [M+Na^+], 417 (33) [M+K^+].

12b: ^{1}H NMR: δ = 0.01, 0.04, 0.05 (each s, 12H), 0.88 (m, 21H), 1.24-1.33 (m, 6H), 1.41-1.45 (m, 2H), 1.60 (dd, ^3J (H,H) = 16.3, 6.2 Hz, 3H; C=CCH_3), 2.02-2.05 (m, 1H), 2.11-2.18 (m, 1H), 2.28-2.38 (m, 1H), 2.44-2.58 (m, 2H), 2.60-2.65 (m, 1H), 4.02-4.09 (m, 2H; CHO), 5.29-5.60 (m, 4H; vinyl).

^{13}C NMR: δ = -4.6, -4.3, 13.6, 14.1, 22.6, 24.7, 25.1, 25.8, 31.8, 38.5, 47.8, 52.5, 54.0, 72.7, 73.3, 126.1, 126.4, 128.6, 136.4, 216.5.

ESMS: *m*/*z* (%): 531 (100) [M+Na^+], 547 (17) [M+K^+].

12c: ^{1}H NMR: δ = 0.02, 0.03, 0.05 (each s, 12H), 0.86, 0.89 (each s, 18H), 1.60 (dd, ^3J (H,H) = 16.3, 6.0 Hz, 3H; C=CCH_3), 2.11-2.19 (m, 2H), 2.36-2.60 (m, 4H), 4.00 (q, ^3J (H,H) = 6.9 Hz, 1H; CHO), 4.15 (m, 2H; CH_2O), 5.31-5.65 (m, 4H; vinyl).

^{13}C NMR: δ = -5.3, -5.2, 12.5, 17.9, 24.6, 47.6, 52.8, 54.1, 63.3, 73.1, 126.2, 127.1, 129.6, 132.5, 215.5.

ESMS: *m*/*z* (%): 461 (100) [M+Na^+], 477 (26) [M+K^+].

Compound 7aa (typical procedure for cleavage of TBS ethers). A solution of **12a** (20 mg, 0.052 mmol) in acetonitrile (2 mL) was cooled to 0 °C and 35% hydrogen fluoride-pyridine (300 μL) was added. The mixture was stirred at room temperature for 7 h and then saturated aqueous sodium bicarbonate (5 mL) was poured into the mixture. The aqueous layer was extracted twice with ethyl acetate and the combined organic solutions washed with 0.5 M HCl,

brine and dried over anhydrous sodium sulfate and then concentrated. The residue was chromatographed eluting with ethyl acetate/hexane (1/3) to give the product as a colorless oil (10 mg, 73%).

^{1}H NMR: δ = 0.87 (t, ^{3}J (H,H) = 6.6 Hz, 3H), 1.24-1.38 (m, 8H), 1.59 (dd, ^{3}J (H,H) = 16.9, 6.1 Hz, 3H; C=CCH_3), 2.04-2.38 (m, 7H), 2.71 (m, 1H), 4.04 (m, 1H; CHO), 5.27-5.68 (m, 4H; vinyl).

^{13}C NMR: δ = 14.1, 22.6, 24.2, 28.8, 29.3, 31.8, 32.6, 45.9, 46.4, 53.8, 54.8, 72.2, 126.2, 126.4, 128.9, 135.5, 213.7.

ESMS: *m*/*z* (%): 287 (67) [M+Na^+], 303 (44) [M+K^+], 263 (58) [M-H^+].

7ab: ^{1}H NMR: δ = 0.87 (t, ^{3}J (H,H) = 6.5 Hz, 3H), 1.24-1.41 (m, 6H), 1.46-1.54 (m, 2H), 1.57 (dd, ^{3}J (H,H) = 17.5, 6.1 Hz, 3H; C=CCH_3), 2.08-2.22 (m, 2H), 2.32-2.42 (m, 3H), 2.72 (dd, ^{3}J (H,H) = 18.0, 6.5 Hz, 1H), 4.06 (m, 2H; CHO), 5.26-5.66 (m; 4H, vinyl).

^{13}C NMR: δ = 12.9, 14.0, 22.6, 24.4, 25.1, 31.7, 37.4, 46.1, 53.7, 54.7, 71.9, 73.1, 126.0, 126.3, 131.7, 136.9, 214.1.

ESMS: *m*/*z* (%): 303 (100) [M+Na^+], 319 (27) [M+K^+].

7ac: ^{1}H NMR: δ = 1.60 (dd, ^{3}J (H,H) = 15.9, 6.4 Hz, 3H; C=CCH_3), 2.11-2.21 (m, 2H), 2.32-2.46 (m, 3H), 2.73 (dd, ^{3}J (H,H) = 17.4, 7.4 Hz, 1H), 4.08 (q, ^{3}J (H,H) = 7.7 Hz, 1H; CHO), 4.17 (m, 2H; CH_2O), 5.26-5.66 (m, 3H; vinyl), 5.83 (m, 1H; vinyl).

^{13}C NMR: δ = 12.9, 24.3, 46.3, 53.3, 54.7, 63.0, 71.9, 125.9, 126.5, 131.5, 132.8, 214.1.

ESMS: *m*/*z* (%): 211 (13) [M+H^+], 209 (10) [M-H^+].

For the synthesis of **7ad**, refer to Figure 1, scheme 2 (supporting information) and the following procedures.

Compound p5ad. A 25 mL rbf containing polymer **3d** (0.47 g, 0.14 mmol) was dissolved in dry THF (14 mL), purged with argon and placed in a cooling bath at -23 °C. The solution was treated with MeLi (1.4 M in hexane, 0.39 mL, 0.56 mmol) added in one portion. Stirring was continued for 40 min at -23 °C and then the yellow solution was rapidly cooled to -78 °C and

treated with the freshly prepared triflate **4a** solution (2.52 mmol) *via* cannula. The resulting solution was stirred for 10 min at -78 °C and for 40 min at -23 °C and then quenched with saturated aqueous ammonium chloride (5 mL) and worked-up according to the same procedure as **pool 5A**. The polymer-supported product (0.38 g, 80% polymer recovered) was obtained as a solid using the standard procedure (*vide supra*).

^{1}H NMR: δ = 3.46 (m, 2H; CH_2Ph), 4.94 (m, 1H; OCHO), 5.4-5.98 (m, 2H; vinyl).

Compound p6ad. The **p5ad** (0.36 g, 0.11 mmol) was dissolved in benzene (3 mL) and cyclohexane (3 mL). To the solution was added quinoline (0.7 g) and 5% palladium on barium sulfate (0.7 g) and the mixture stirred under hydrogen (1 atm) at 45 °C for 48 h. The catalyst was filtered through a pad of Celite and the filtrate evaporated. The polymer-supported product (0.32 g, 90% polymer recovered) was obtained as a solid using the standard procedure (*vide supra*).

^{1}H NMR: δ = 3.4 (m, 2H; CH_2Ph), 4.91 (m, 1H; OCHO), 5.25-5.92 (m, 4H; vinyl).

Compound 7ad. A solution of **p6ad** (0.3 g, 0.09 mmol) in THF (3.5 mL) was treated with 48% aqueous hydrofluoric acid (0.45 mL). The mixture was stirred at 45 °C for 6 h and then neutralized with saturated sodium bicarbonate solution. The aqueous layer was extracted with ethyl acetate and the organic solution was washed with saturated sodium bicarbonate, brine and dried over anhydrous sodium sulfate and then concentrated. To the residue was added a small amount of THF (0.2 mL) and MeOH (10 mL) and the mixture cooled to -30 °C with vigorous stirring to precipitate the polymer. After removal of the polymer, the filtrate was concentrated to give the crude product. The residue was chromatographed eluting with ethyl acetate/hexane (1/1) to give the product as a colorless oil (8 mg, 32%).

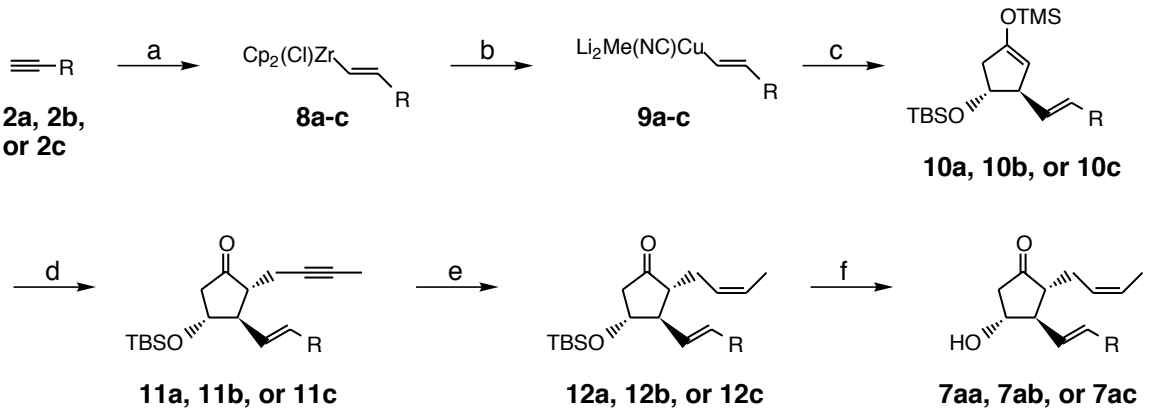
^{1}H NMR: δ = 1.56 (dd, ^3J (H,H) = 30.7, 6.8 Hz, 3H; C=CCH_3), 2.0-2.23 (m, 3H), 2.34-2.45 (m, 2H), 2.73 (dd, ^3J (H,H) = 18.5, 7.3 Hz, 1H), 3.40 (d, ^3J (H,H) = 6.5 Hz, 2H; CH_2Ph), 4.07 (q, ^3J (H,H) = 9.2 Hz, 1H; CHO), 5.27-5.85 (m, 4H; vinyl), 7.18-7.29 (m, 5H; aromatic).

^{13}C NMR: δ = 12.9, 24.4, 39.0, 46.2, 53.3, 54.7, 72.1, 126.1, 126.2, 126.3, 128.4, 128.5, 130.5, 133.7, 139.9, 214.3.

ESMS: *m*/*z* (%): 293 (44) [M+Na^+], 309 (56) [M+K^+].

Biological Assay of MCMV Growth in NIH 3T3 Cells. Murine NIH 3T3 fibroblasts (ATCC CRL 1658) were infected with RM461 murine cytomegalovirus recombinant [C. A. Stoddart, R. D. Cardin, J. M. Boname, W. C. Manning, G. B. Abenes, E. S. Mocarski, *J. Virol*. **1994**, *68*, 6243-6253] at a multiplicity of infection of 0.05 PFU/cell in Dulbecco's modified essential medium supplemented with 2 mM glutamine, 100 U of penicillin/mL, 100 μg of gentamicin/mL, and 3% charcoal resin-treated calf serum. Infections were carried out at 37 °C and 7% carbon dioxide. After a 1 h adsorption period, virus inoculum was removed, the cultures washed three times with phosphate-buffered saline and fresh medium added containing the prostanoid(s) in dimethyl sulfoxide (or dimethyl sulfoxide alone for the control) at a concentration of 20 μM. On day three after infection, the supernatant of two independent cultures were harvested, frozen, thawed, and infectious virus quantitated by a standard plaque assay on NIH 3T3 cells [A. R. Brautigam, F. J. Dutko, L. B. Olding, M. B. A. Oldstone, *J. Gen. Virol*. **1979**, *44*, 349-359].

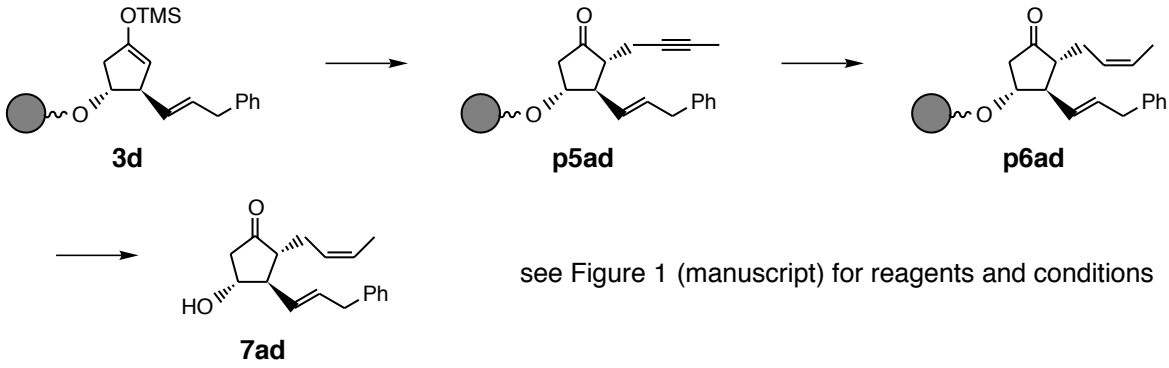
Scheme 1



2a, 2b, or 2c | **8a-c** | **9a-c** | **10a, 10b, or 10c** | **11a, 11b, or 11c** | **12a, 12b, or 12c** | **7aa, 7ab, or 7ac**

a) $Cp_2Zr(H)Cl$ (2 eq.), THF, rt, 30 min; **b**) i) MeLi (4 eq.), -50 ^{o}C, 10 min, ii) CuCN (2 eq.), -50 ^{o}C, 15 min, then MeLi (2 eq.), -50 ^{o}C, 15 min; **c**) i) (R)-(+)-4-(t-butyldimethylsilyloxy)-2-cyclopentene-1-one (3 eq.), THF, -50 ^{o}C, 15 min, ii) TMSCl (5 eq.), -50 ^{o}C, 30 min, then NEt_3 (10 eq.), -50 ^{o}C to 0 ^{o}C, 15 min; **d**) i) MeLi (1.5 eq.), THF, -23 ^{o}C, 15 min, ii) **4a** (6 eq.), THF, -78 ^{o}C, 10 min, then -23 ^{o}C, 20 min; **e**) H_2, 5% Pd-$BaSO_4$, quinoline, benzene/cyclohexane (1:1), rt, 2.5 hr, then 45 ^{o}C, 3 h; **f**) HF-pyridine, acetonitrile, rt, 6 h.

Scheme 2



see Figure 1 (manuscript) for reagents and conditions